

High Temperature Aerogels in the Al_2O_3 - SiO_2 System

Al_2O_3 - SiO_2 aerogels are of interest as constituents of thermal insulation systems for use at high temperatures. Al_2O_3 and mullite aerogels are expected to crystallize at higher temperatures than their SiO_2 counterparts, hence avoiding the shrinkages that accompany the formation of lower temperature SiO_2 phases and preserving pore structures into higher temperature regimes. The objective of this work is to determine the influence of processing parameters on shrinkage, gel structure (including surface area, pore size and distribution) and pyrolysis behavior.

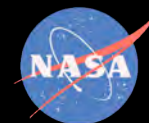
HIGH TEMPERATURE AEROGELS IN THE $\text{Al}_2\text{O}_3\text{-SiO}_2$ SYSTEM

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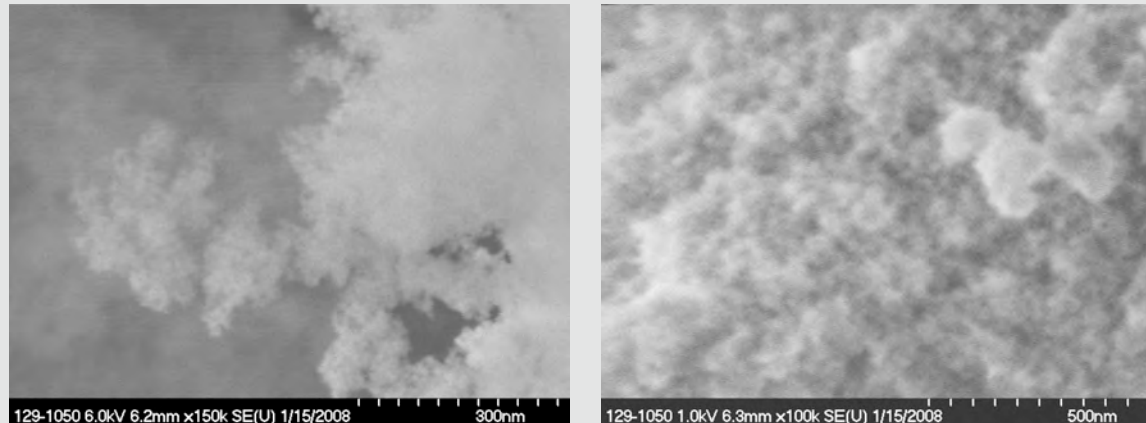
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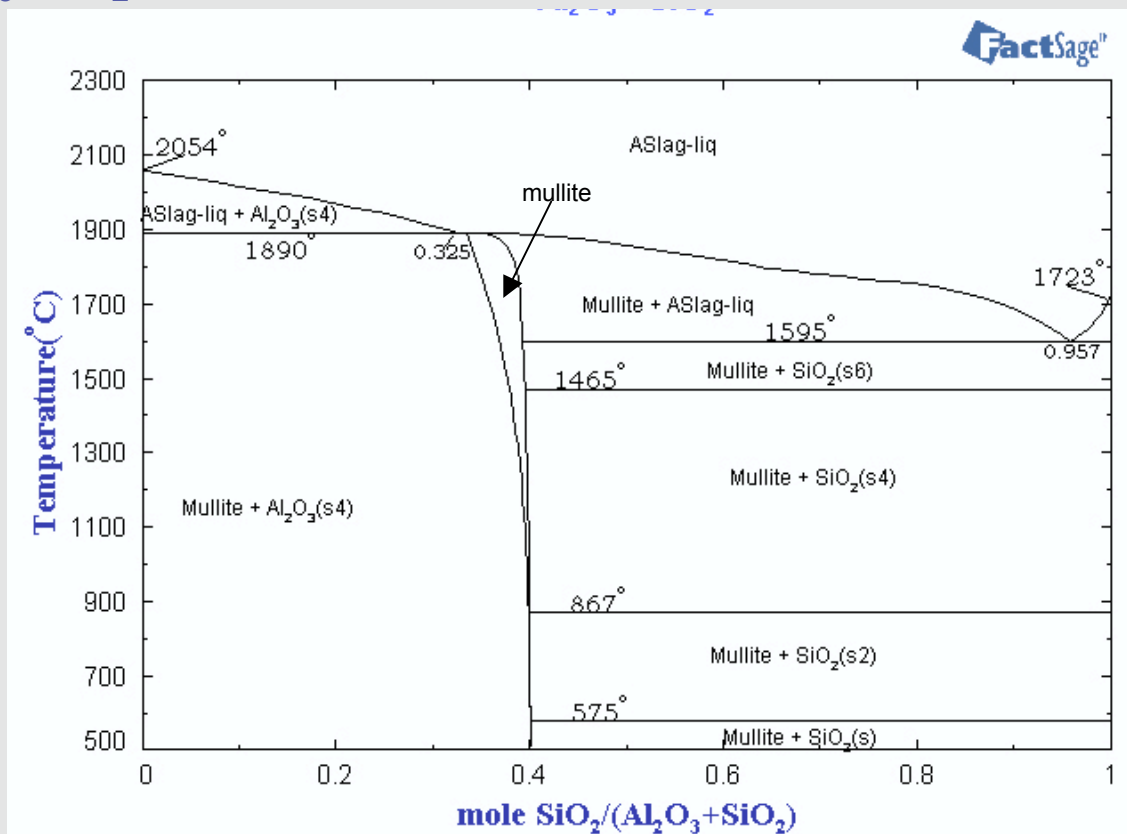
Objective:

- To explore the use of high temperature aerogels in the development of lightweight, insulating materials for application temperatures $> 1000\text{ C}$.
 - To develop an understanding of the interrelationships among stoichiometry, processing parameters, morphology and thermal behavior to achieve the temperature goal.



$3\text{Al}_2\text{O}_3\text{-}2\text{SiO}_2$ (3Al:1Si) aerogel maintains fractal structure following brief exposure at 1050C .

Al₂O₃-SiO₂ Phase Diagram-- Target compositions shown by arrows.



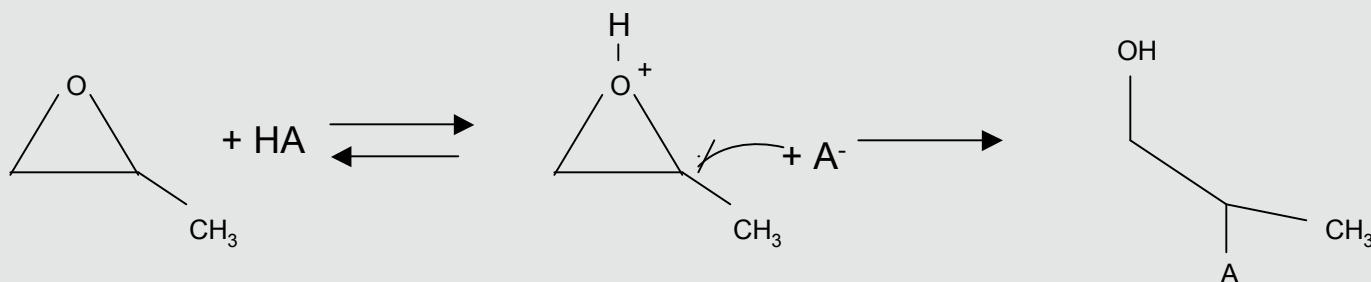
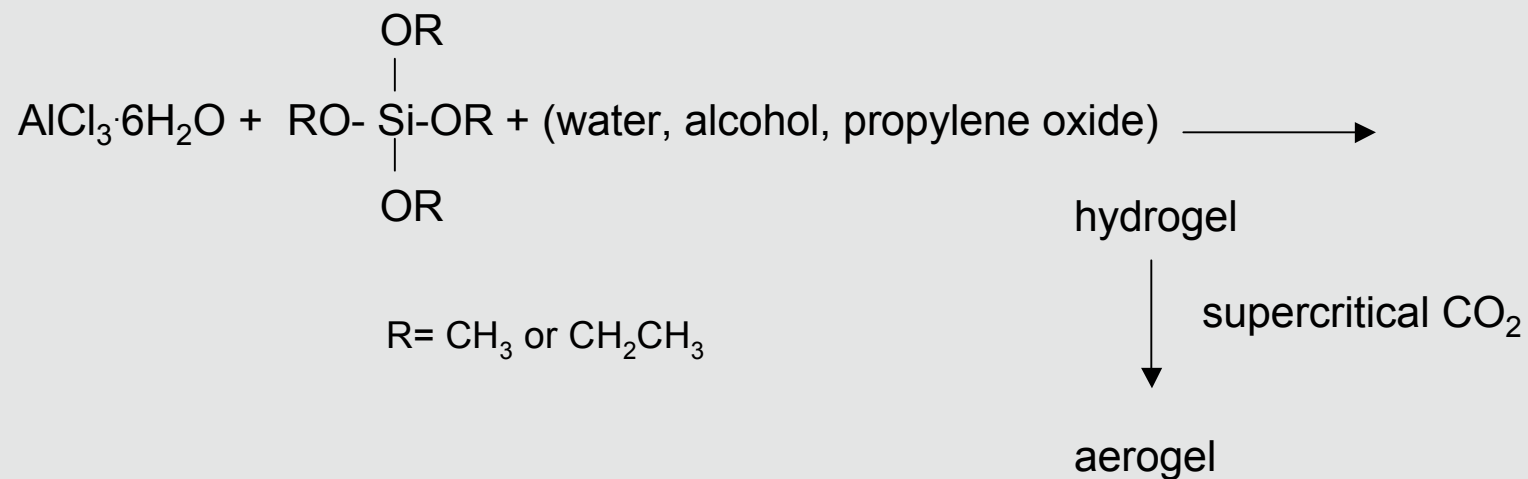
↑
1 Al: 0Si

↑
8:1 Al:Si

↑
3:1 Al:Si
(3:2 mullite)

↑
1:1 Al:Si

Synthesis approach:



- B. J. Clapsaddle, *et al.*, *J. Non-Crystalline Solids* **350**, 173-181 (2004).

Variables:

Al/Si ratio

water/ M

alcohol/ M

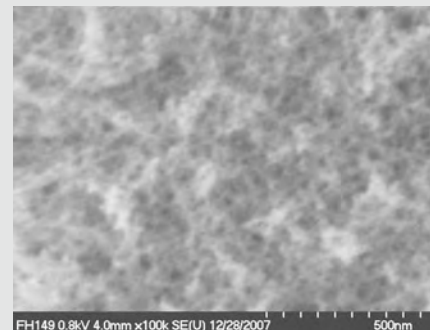
solids loading

hydrolysis time

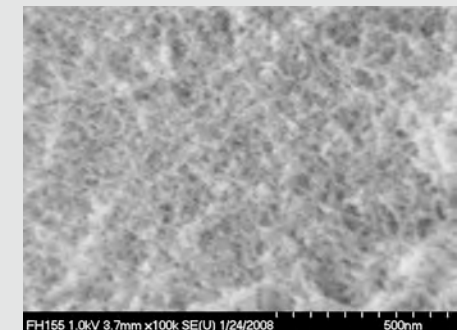
chilling/addition of reactants

Determine influence of processing parameters on shrinkage, gel structure (surface area, pore size and pore distribution, density and pyrolysis behavior.

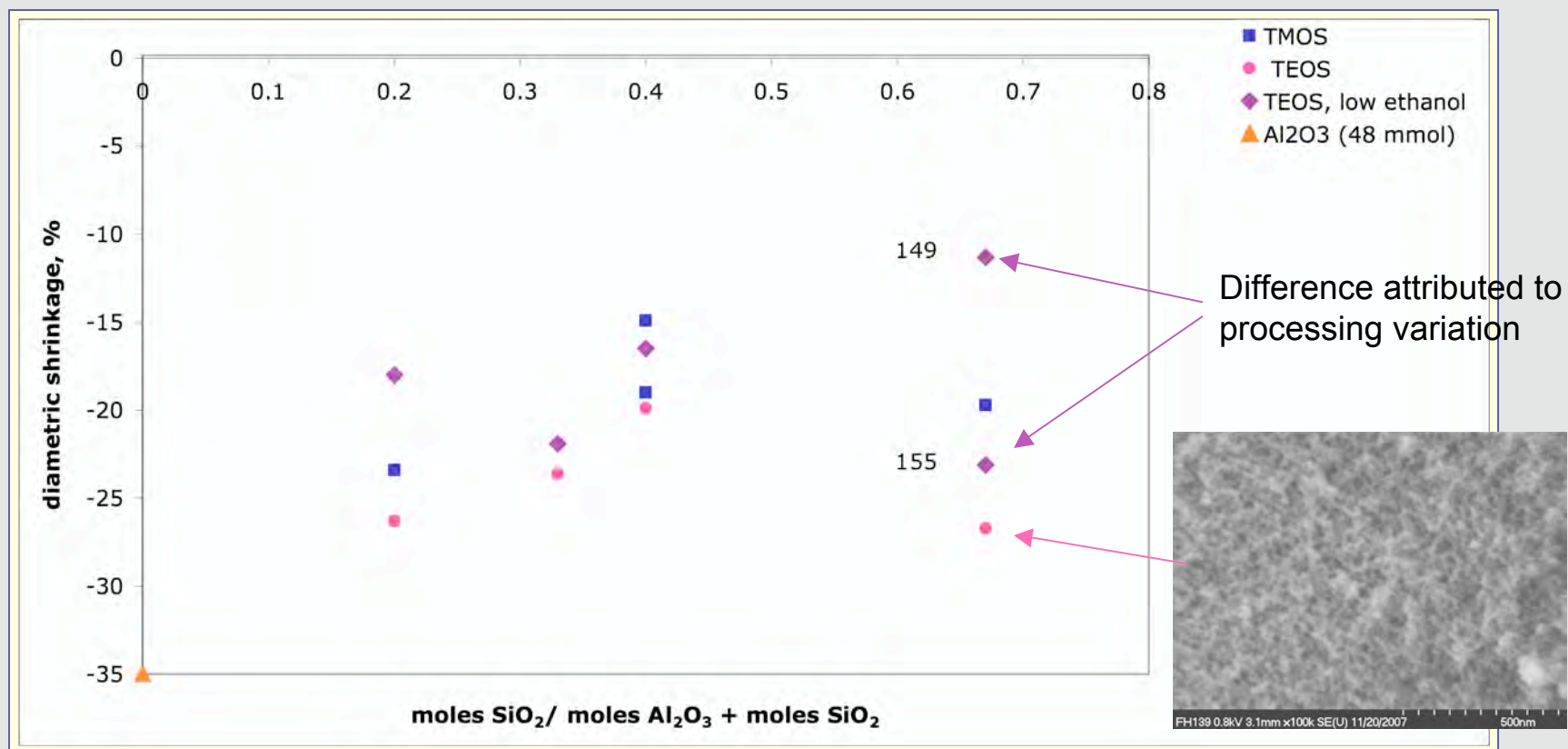
- In early experiments, samples chilled directly in dry ice prior to addition of propylene oxide to slow gelation; pore structure varied with chilling time
- Reducing ethanol reduces shrinkage, but requires tighter process control.

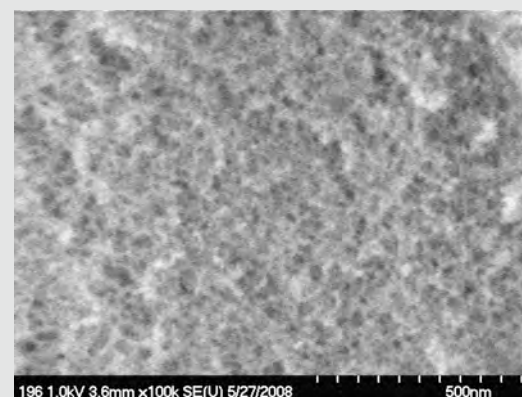
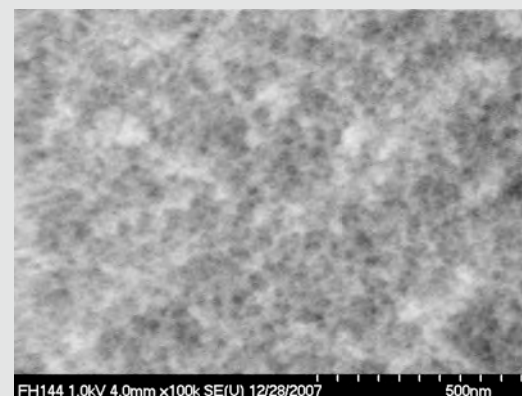
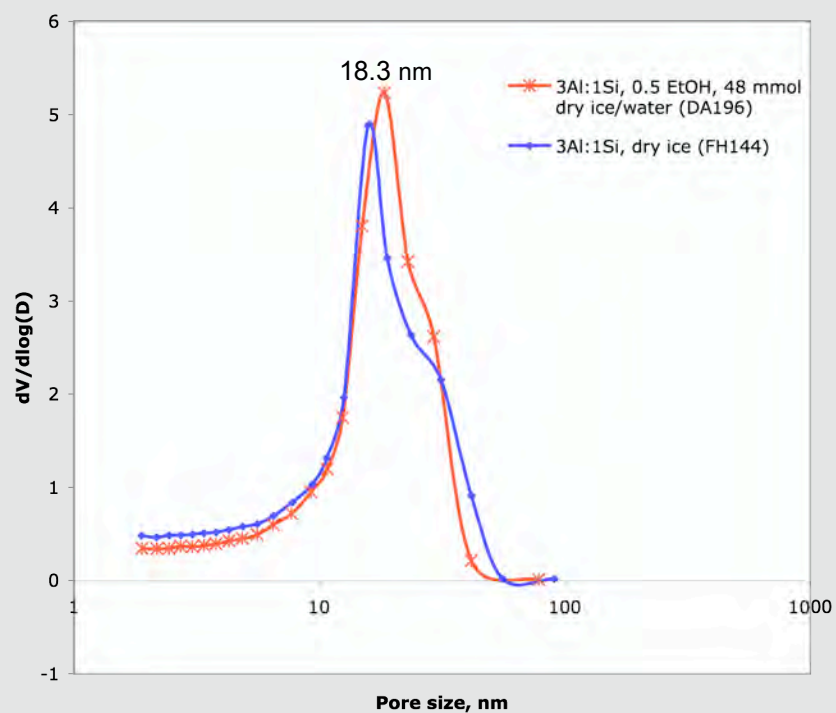
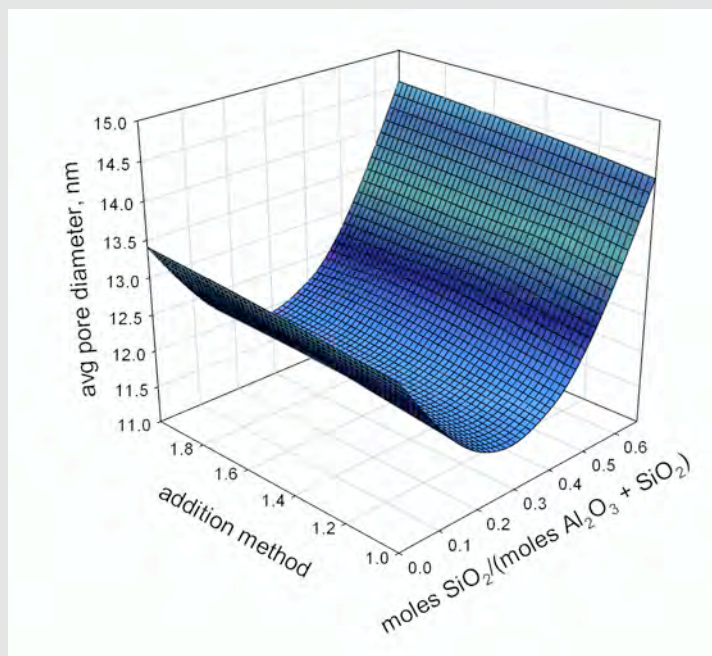


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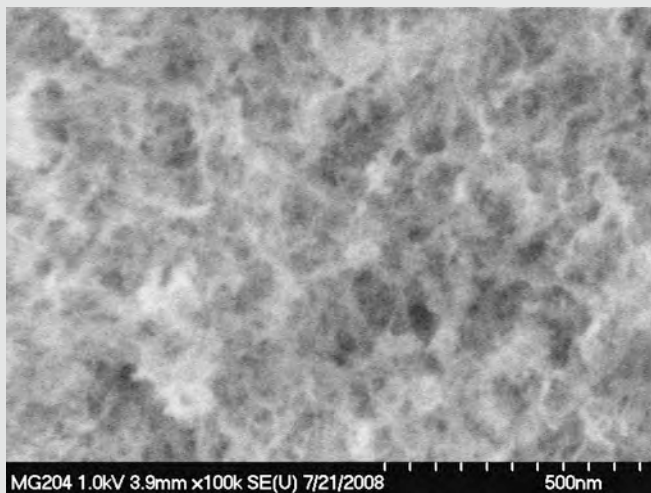
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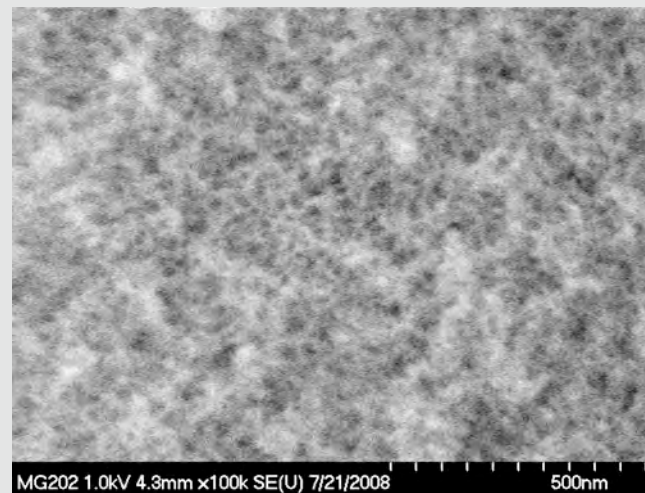


3Al:1Si--gels. Chilled on dry ice, top, and in dry ice/water bath, bottom.

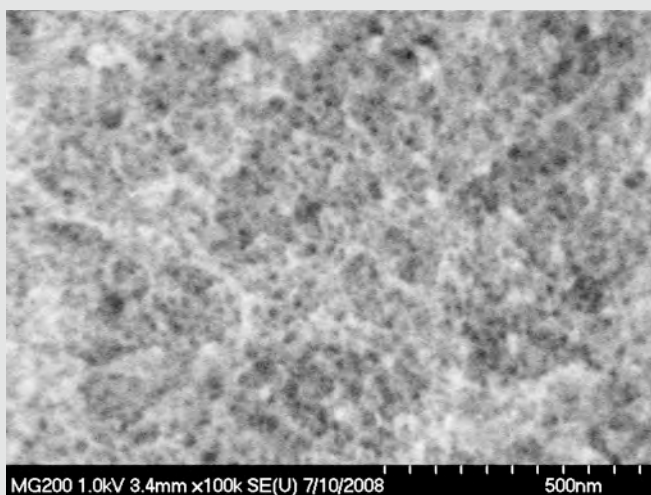
- Change in chill method improves process control, with slight increase in average pore diameter and slight decrease in surface area.
- Pore size is governed primarily by stoichiometry, with smallest average pore diameter at 3Al:1Si composition.



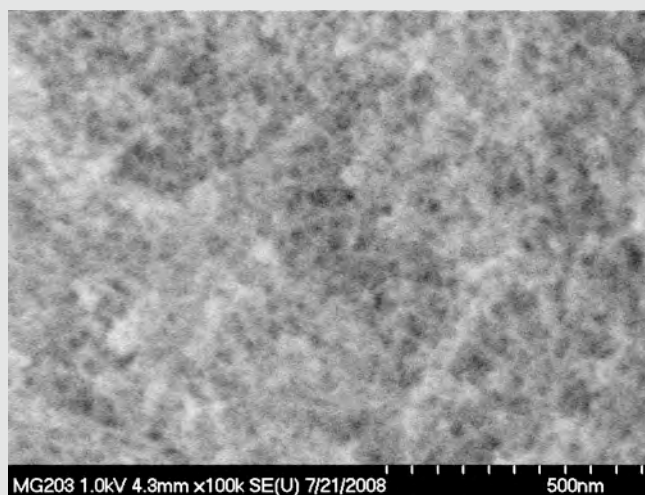
1Al:0Si, low solids, 0.5 EtOH



8Al:1Si, low solids, 0.5 EtOH

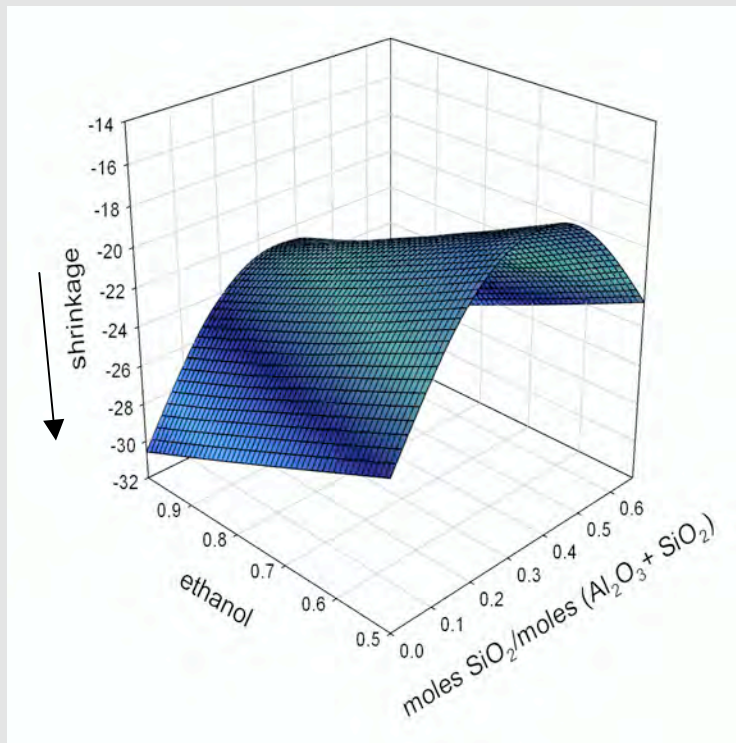


3Al:1Si, low solids, 0.5 EtOH



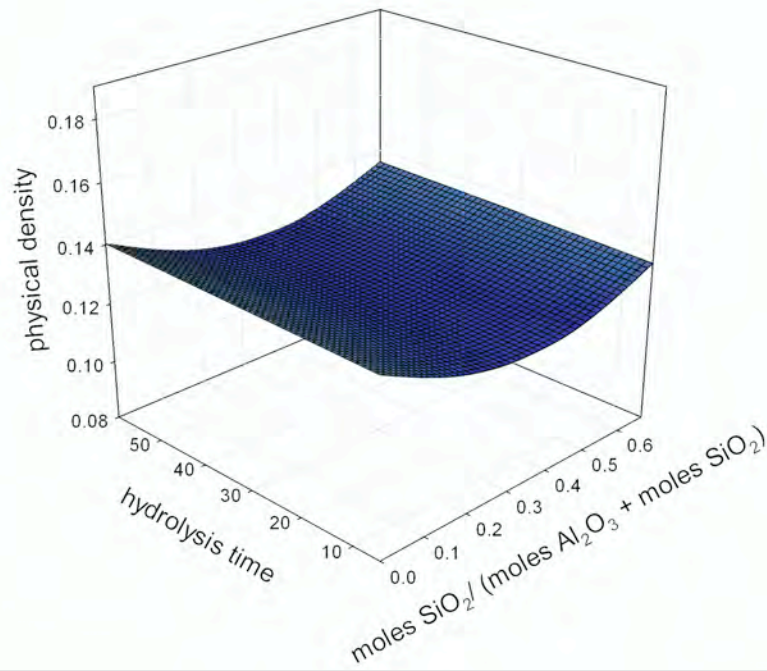
1Al:1Si, low solids, 0.5 EtOH

Pore size distribution varies with composition.

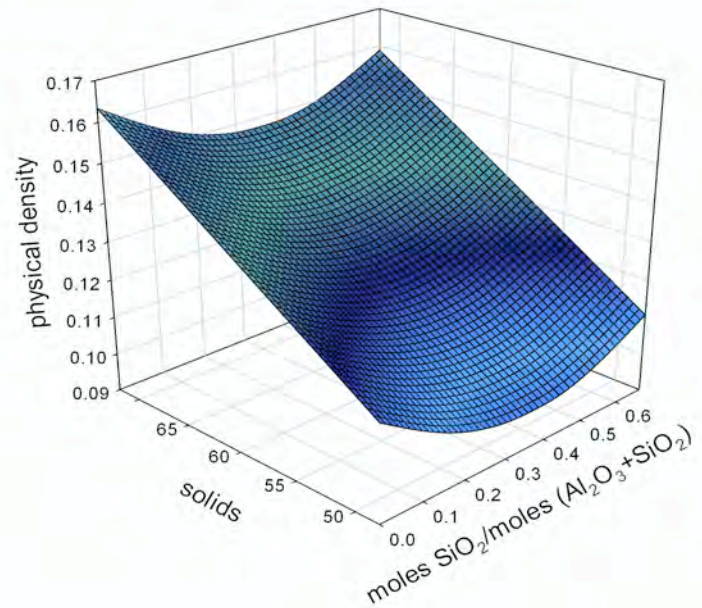
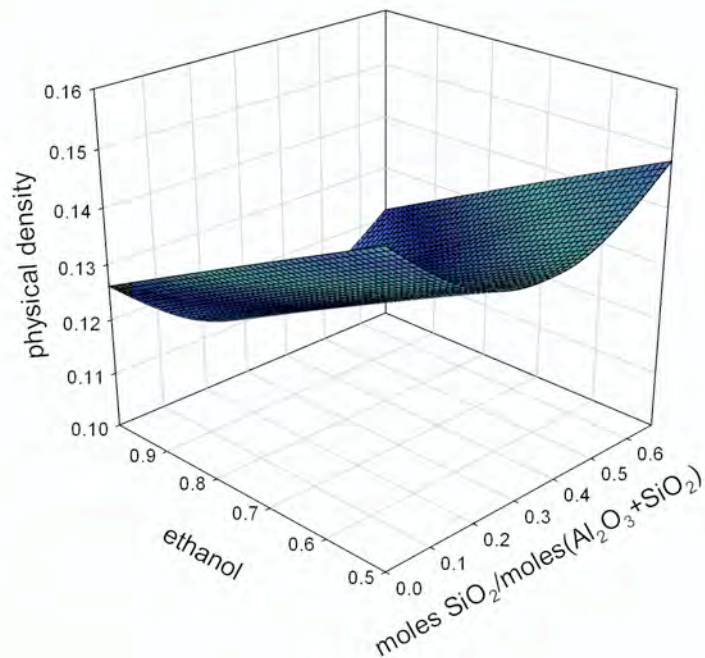


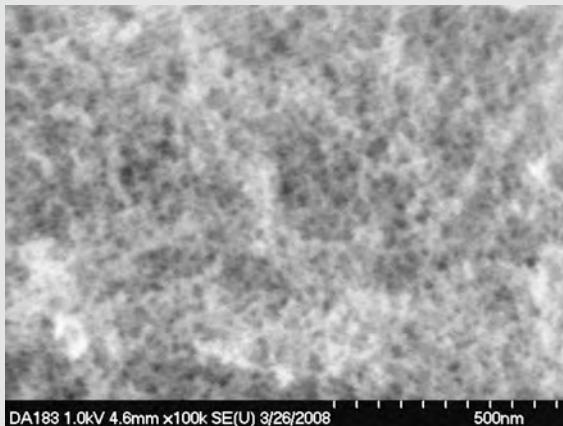
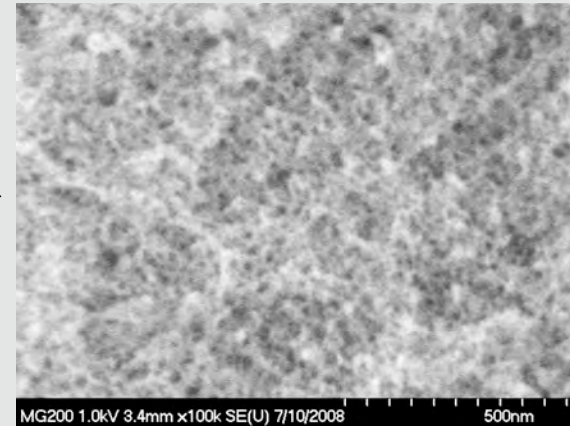
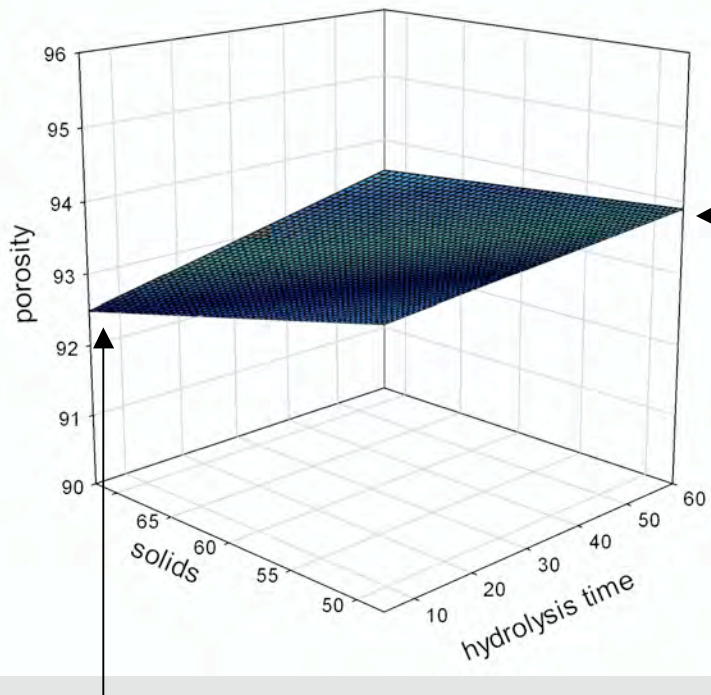
Shrinkage control is important to integrating aerogels with structure

- Shrinkage expressed as percent linear change in diameter of cylindrical gel, and includes shrinkages on both aging of hydrogel and in supercritical drying.
- Shrinkage at minimum for 3Al:1Si composition.
- Maximum shrinkage observed in Al₂O₃ aerogel at high ethanol level.
- At each composition, shrinkage increases with increased ethanol concentration.

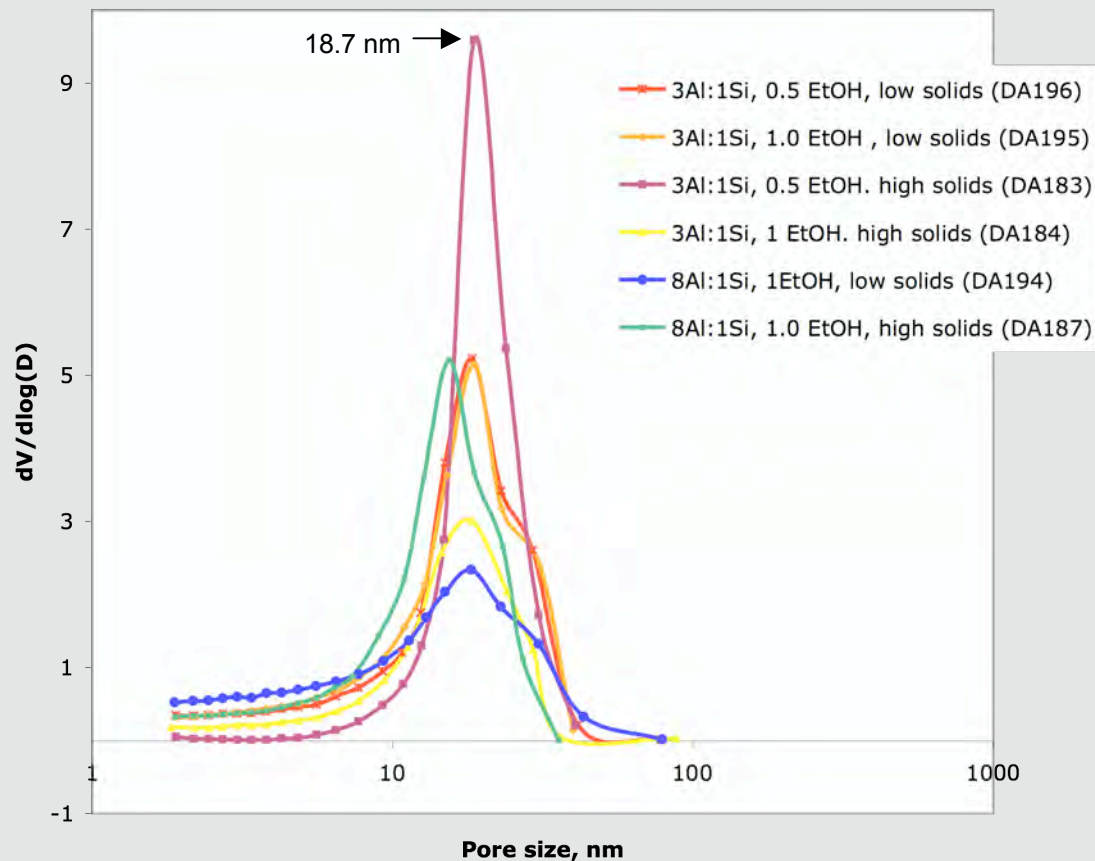


- Physical density is lowest at 3Al:1Si composition.
- Density increases slightly with hydrolysis time, decreases with ethanol concentration, and increases sharply with solids loading.



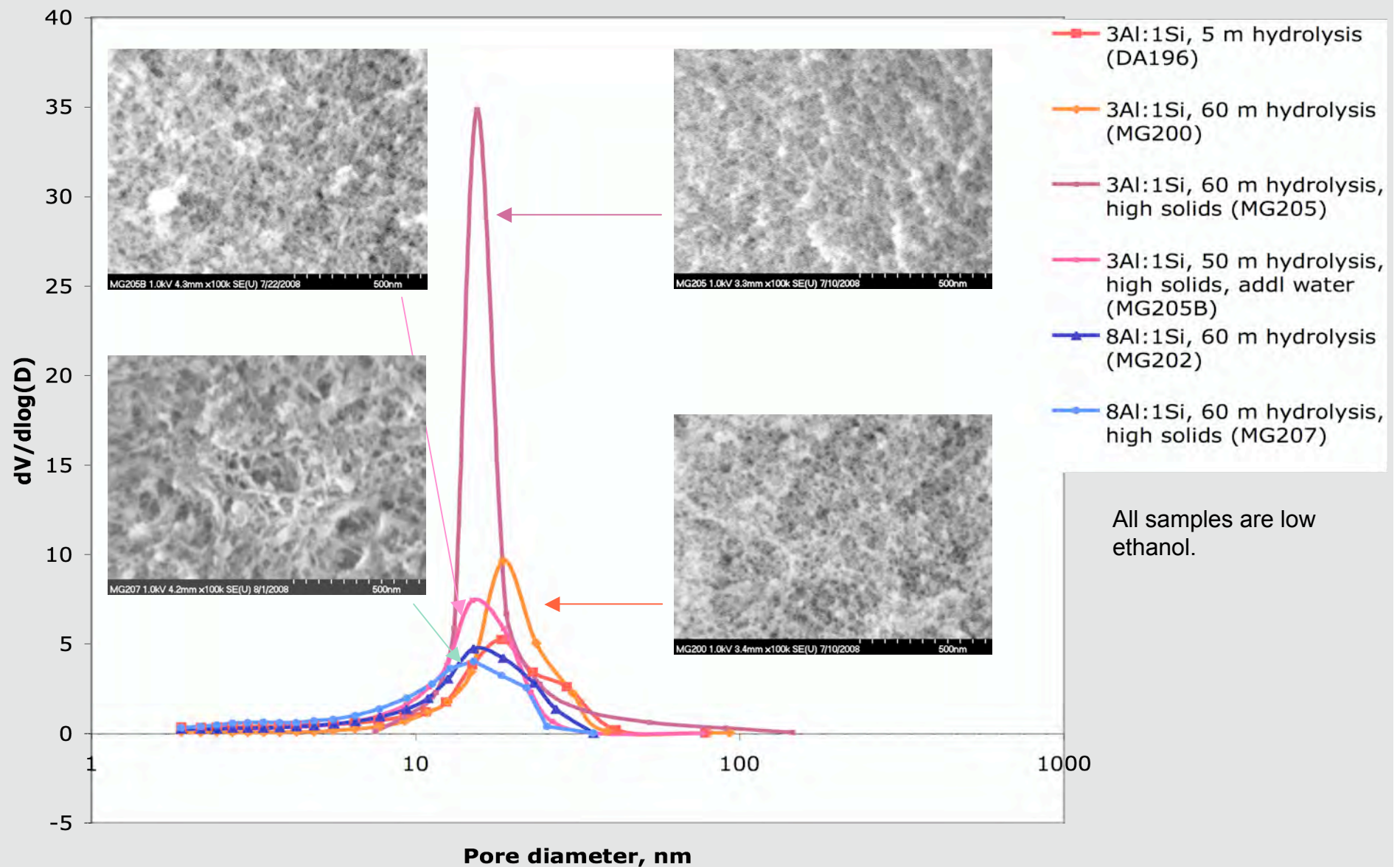


- Porosity ranges from 90-96 percent.
- Porosity varies with hydrolysis time and solids loading.
- Only small difference in pore size distribution observed in 3Al:1Si composition at extremes of porosity range.



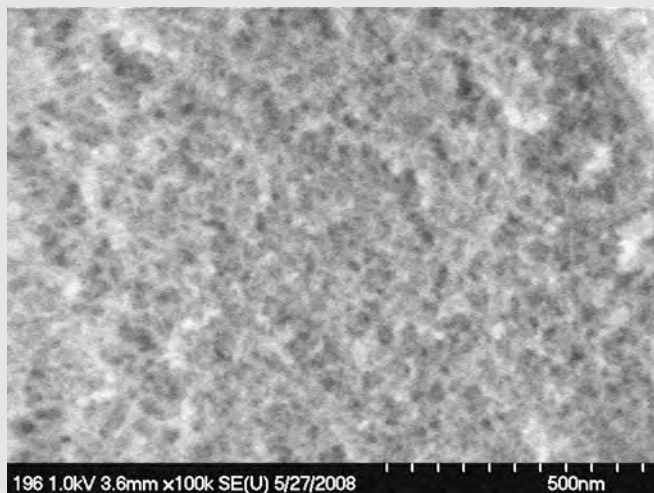
Pore size distribution as determined by N₂ desorption

- 3Al:1Si shows little variation in pore size distribution with ethanol concentration at low solids loading.
- Distribution narrows and population of 15-18 nm pores increases with solids loading. *(Please note scale for comparison with next slide).*

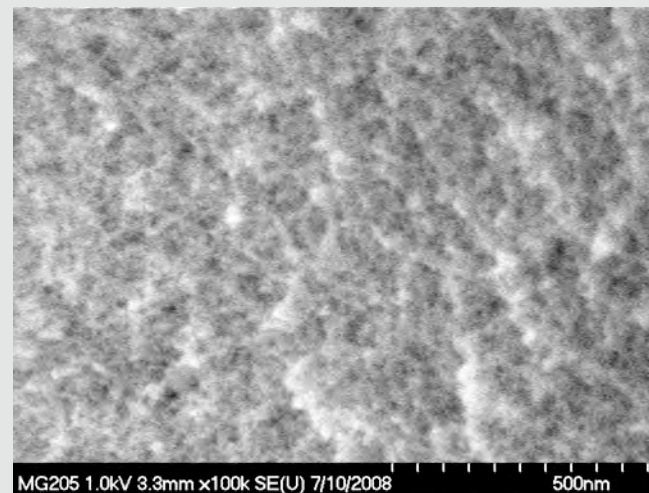


All samples are low ethanol.

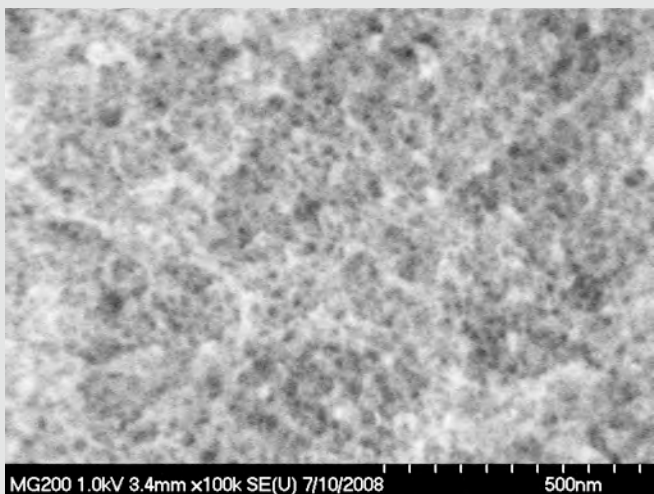
- Longer hydrolysis time increases number of small pores (note change in scale from previous slide).
- 8Al:1Si, high solids sample exhibits “strut-like” morphology.



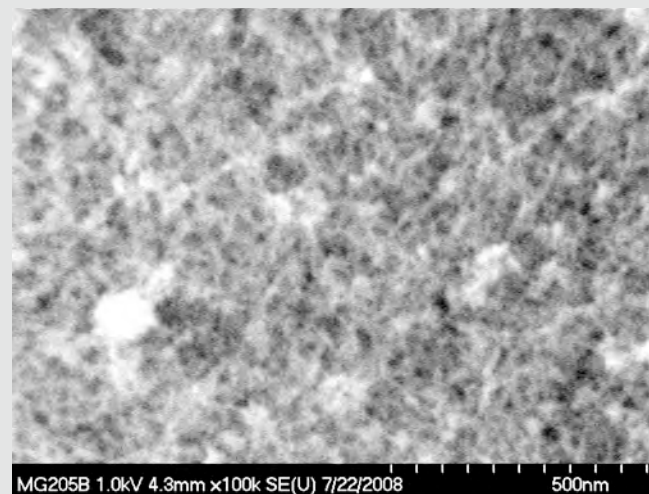
196 1.0kV 3.6mm x100k SE(U) 5/27/2008 500nm
 3Al:1Si, 0.5 EtOH, low solids, 5min hydrolysis. BET=641 m²/g



MG205 1.0kV 3.3mm x100k SE(U) 7/10/2008 500nm
 3Al:1Si, 0.5 EtOH, high solids, 60 min hydrolysis. BET=796 m²/g

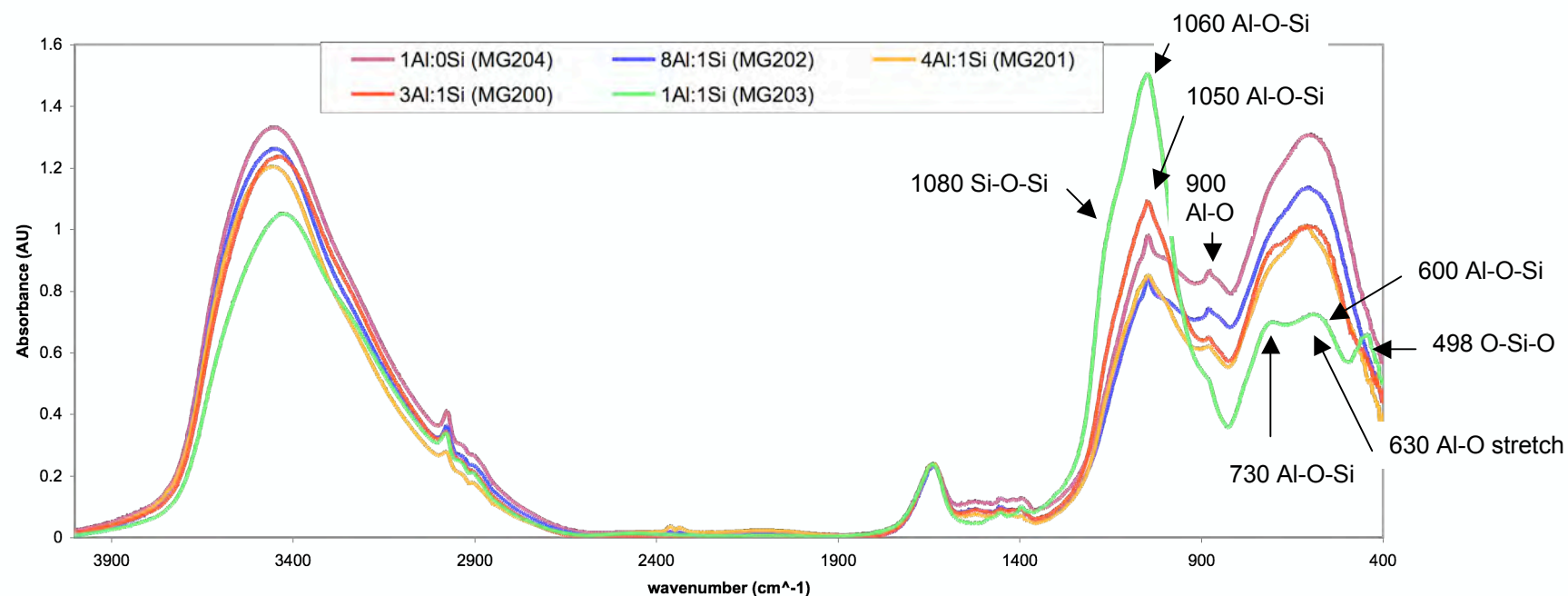


MG200 1.0kV 3.4mm x100k SE(U) 7/10/2008 500nm
 3Al:1Si, 0.5 EtOH, low solids, 60 min hydrolysis. BET=514 m²/g

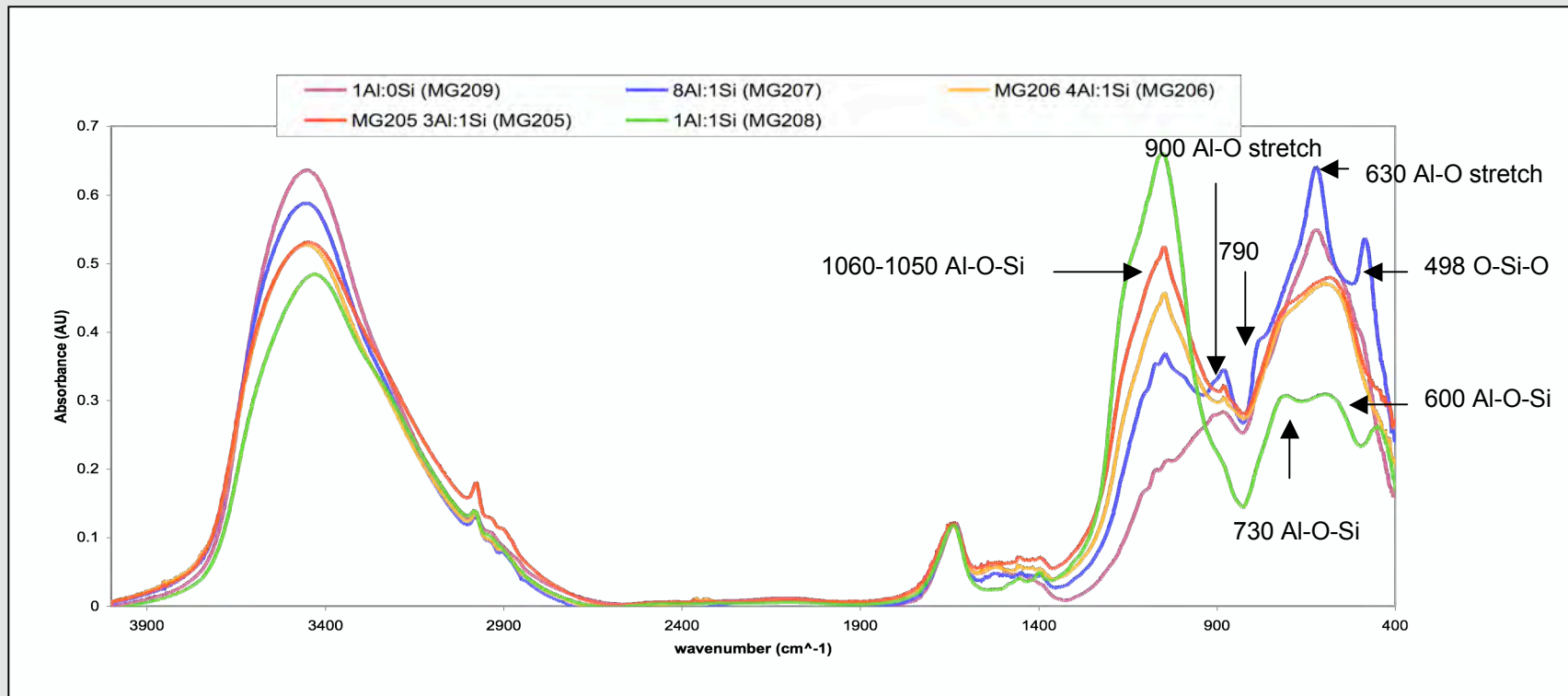


MG205B 1.0kV 4.3mm x100k SE(U) 7/22/2008 500nm
 3Al:1Si, 0.5 EtOH, high solids, added water, 60 min hydrolysis. BET=685 m²/g
 (Water/functional group ratio in 205B matches MG200)

FTIR Spectroscopy is characterized by overlapping Si-O-Si, Al-O-Al and Al-O-Si bands which vary in intensity with composition. (Low solids gels shown).

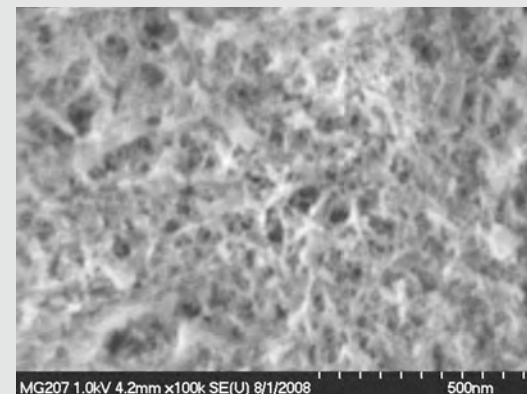


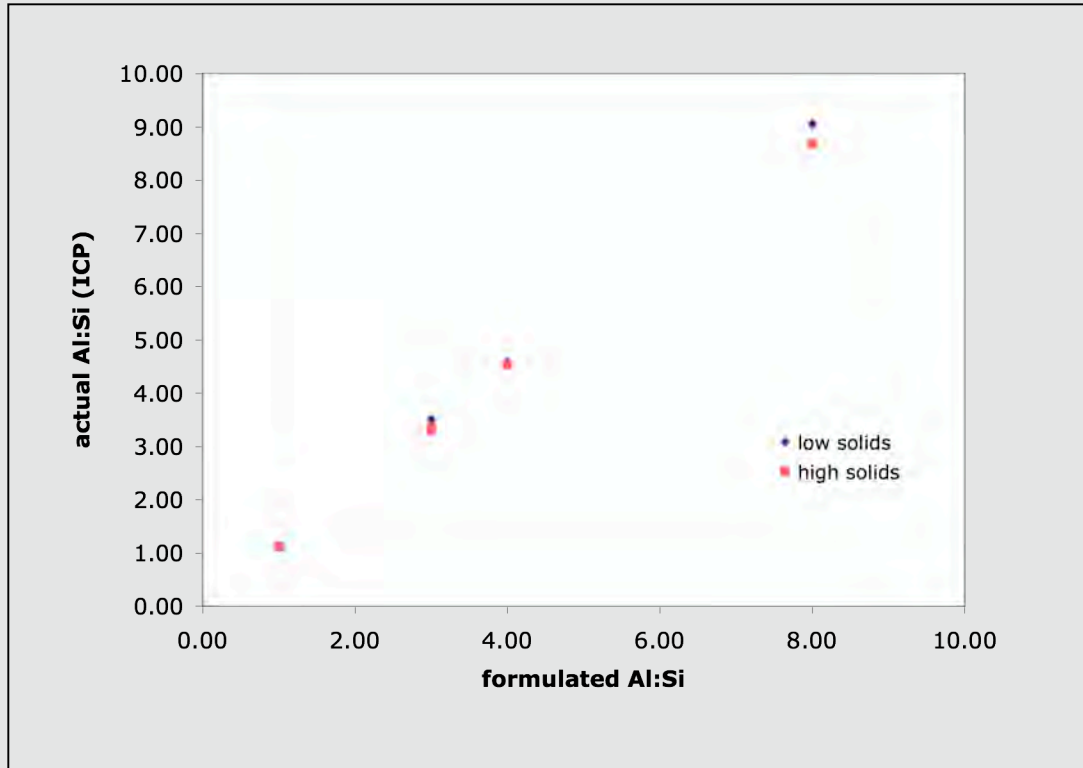
- Peak at 1060 cm^{-1} (Al-O-Si) and shoulder at 1080 cm^{-1} decreases with Al
- Peak at 900 cm^{-1} (Al-O stretch) increases as Al increases
- Peak at 730 cm^{-1} more prominent (O-Al-O bend) with decreasing Al, as 600 cm^{-1} (Al-O-Si) decreases



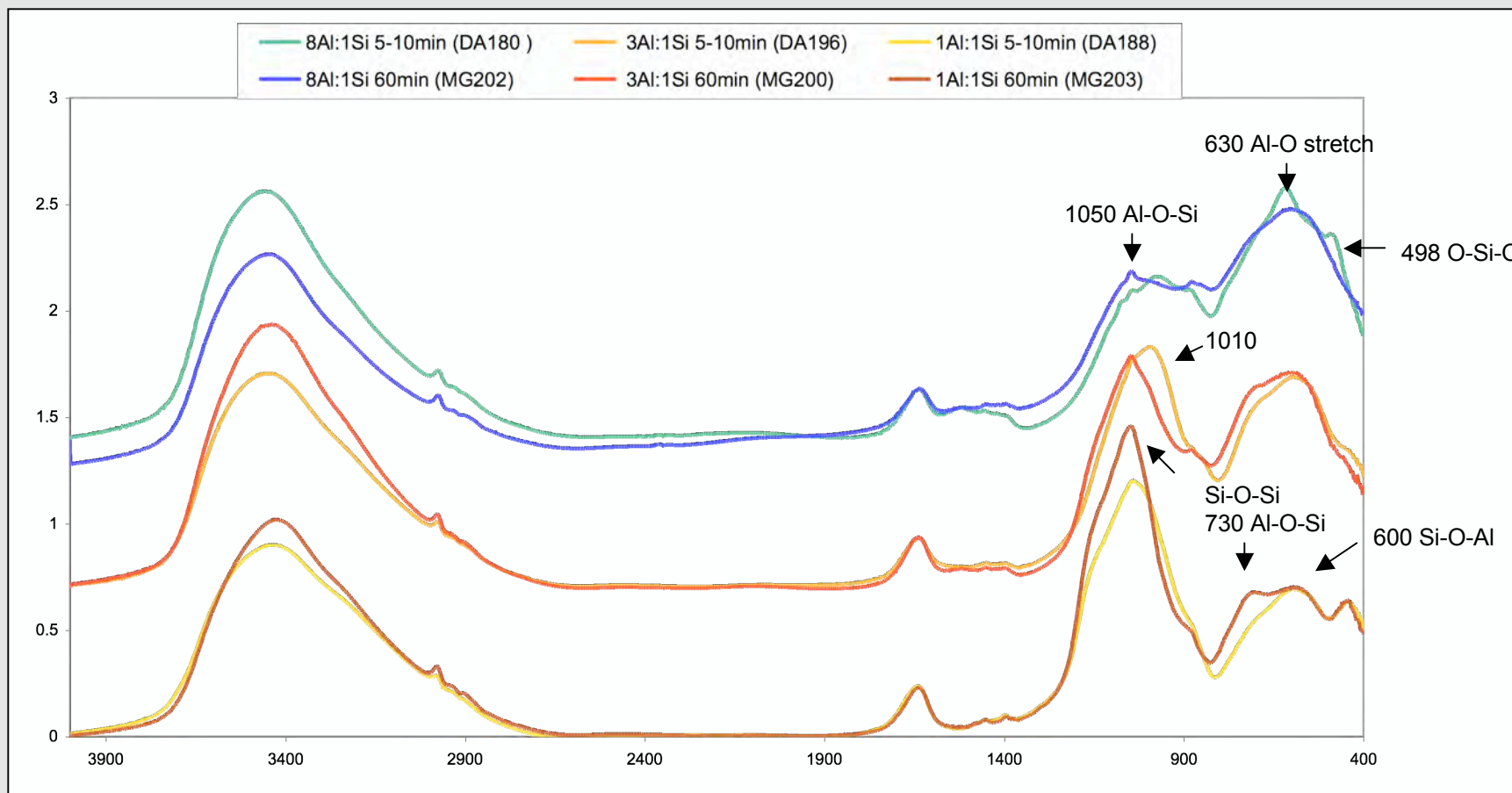
FTIR Spectroscopy of high solids samples shows Al-O stretch at 900 and 630 cm⁻¹ in all Al₂O₃ and 8Al:1Si gels to be more prominent than in low solids samples, having less Al-O-Si bonding.

8Al:1Si sample exhibited large pores and strut-like morphology.





ICP analysis indicates Al:Si ratio to be slightly higher than formulated ratio, but does not account for differences in FTIR spectra.



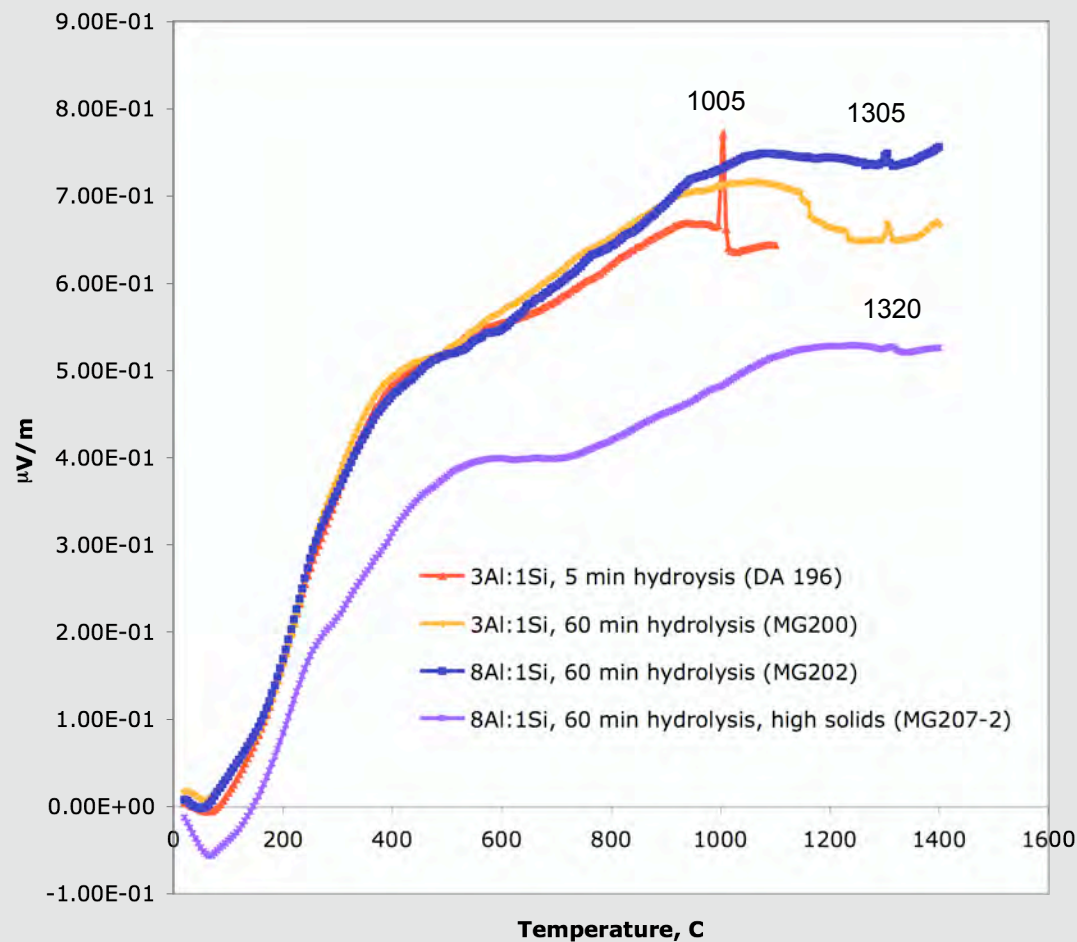
- FTIR Spectroscopy suggests formation of Al-O-Si in network increases with hydrolysis time:

Al-O-Si bands: 1060-1050 cm⁻¹ [1], 700 cm⁻¹ and 600 cm⁻¹ [2]

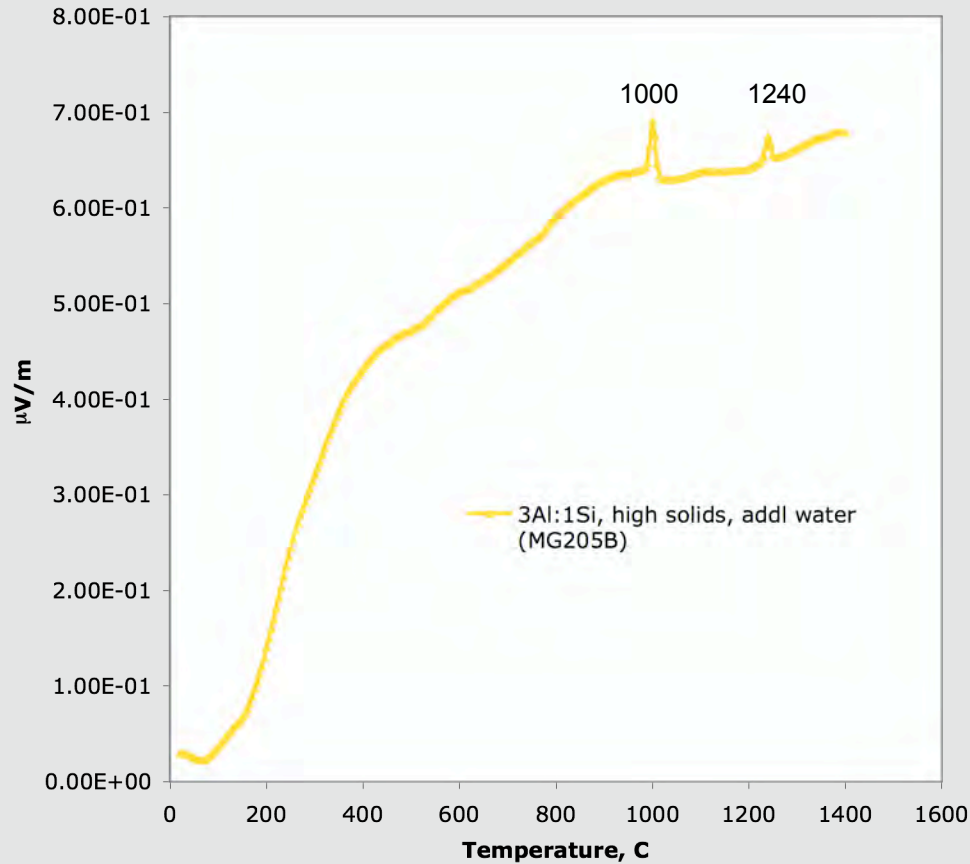
- ²⁷Al and ²⁹Si NMR planned to confirm interpretation

[1] Sigurdur Jakobsson, "Determination of Si/Al Ratios in Semicrystalline Aluminosilicates by FT-IR Spectroscopy", *Spectroscopic Techniques* **56(6)**, 797-9, 2002.

[2] K. Sinko, R. Mezei, J. Rohonczy, P. Frazl, "Gel Structures Containing Al(III)," *Langmuir* **15**, 6631-6636, 1999.



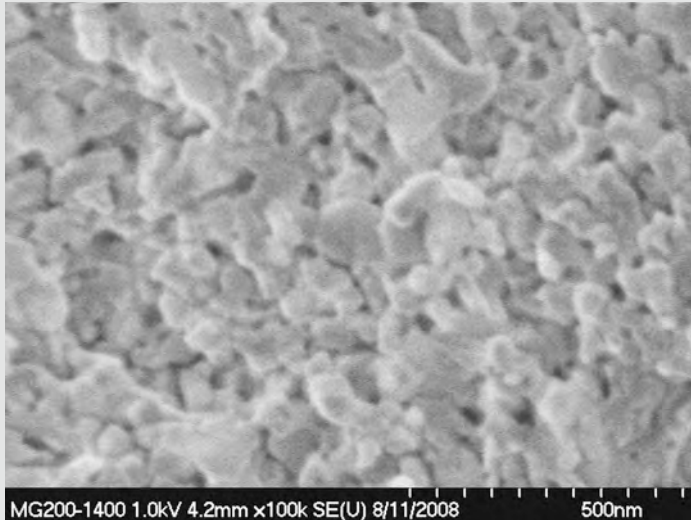
Differential thermal analysis (DTA) in He shows characteristic crystallization peak at at 1005 C for 3Al:1Si gels at short hydrolysis times; peak shifts to >1300 C with longer hydrolysis. In 8Al:1 Si gels, crystallization peak occurs at 1305 C with low solids, increasing to 1320 C at higher solids loading.



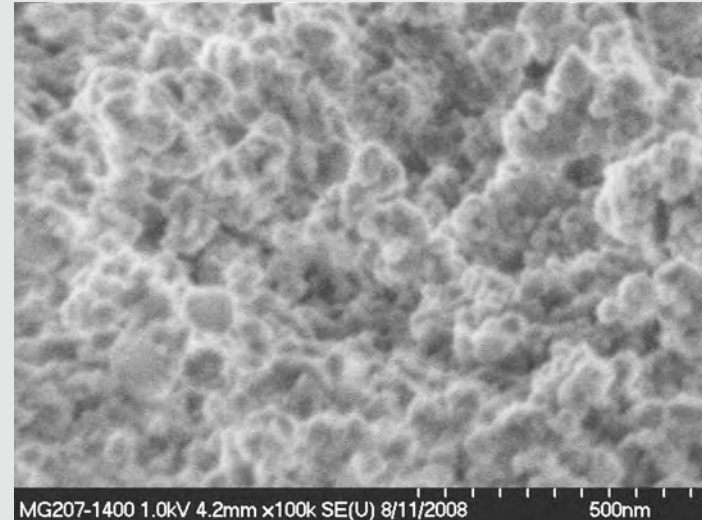
However, at high solids loading the 3Al:1Si gel, with longer hydrolysis time, exhibits crystallization peaks at 1000 and 1240-1245 C.

Mullite + Al_2O_3
(primarily monoclinic,
with possible $\text{Al}_{2.66}\text{O}_4$)

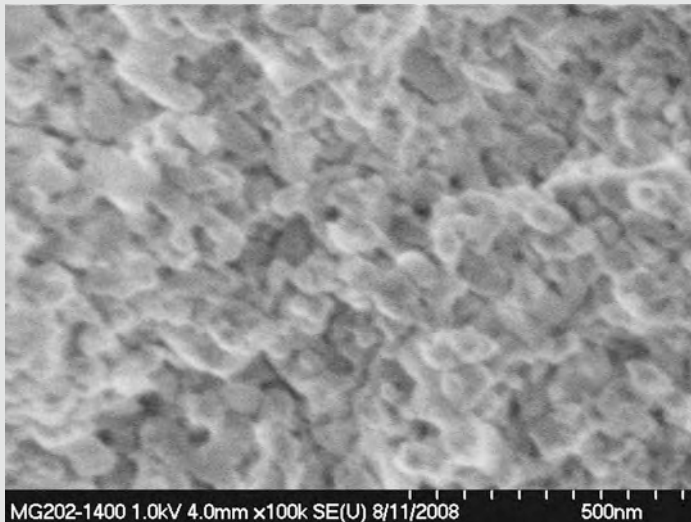




3Al:1Si, low solids, heated to 1400C in He



8Al:1Si, high solids, heated to 1400C in He



8Al:1Si, low solids, heated to 1400C in He

8Al:1Si high solids sample heated to 1400C (above) differs in morphology from low solids 3Al:1Si and 8Al:1Si samples (left), and appears to have lower density structure.

SUMMARY AND CONCLUSIONS

- Aluminosilicates with Al:Si ratios of 3:1 and 8:1 produce aerogels with no excess SiO_2 phase, which crystallize to mullite plus Al_2O_3 phases.
- Shrinkage and density are minimized at a 3Al:1Si composition. This composition also produces the finest pore size microstructure.
- Increasing solids loading increases density, but also increases the population of small pores. Adding water in proportion to increase in solids loading increases pore size.
- Aluminosilicate network structure is affected by hydrolysis time and solids loading.
- Aerogels have been formed which crystallize at temperatures above 1300 C. A full understanding of changes above 1000 C, and of the maximum temperature attainable before the aerogel pore structure is lost, requires additional study.
- Unique, strut-like microstructures have been produced at an 8Al:1Si composition, high solids loading, and with a slight process variation, that crystallize at 1320 C to a mixture of mullite and primarily monoclinic Al_2O_3 , while maintaining a porous morphology. This composition is undergoing further investigation.
- The aluminosilicate aerogels offer a more attractive mix of properties than their all Al_2O_3 counterparts, which undergo high shrinkages, exhibit large pores, and crystallize at 1225-1255 C.

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